10/088260
JC Rec'd PCT/PTO 15 MAR 2002

"Express Mail" mailing label number EL780370457US

WO 01/19952 PCT/EP00/08688

# Detergent Tablets

Background of the Invention

## ~~Field~~ of the Invention

This invention relates generally to shaped detergents and more particularly to tablets containing surfactants, builders and disintegrating agents and, in addition, proteins or protein derivatives as softening agents.

## ~~Prior Art~~

Detergents which not only clean laundry but also give it a particular softness are available on the market. Corresponding preparations, which are often referred to as soft detergents, generally contain cationic surfactants of the tetraalkyl ammonium compound type, mostly in combination with layer silicates, as softeners. The quaternary ammonium compounds mentioned are unsatisfactory in their biodegradability and in addition are known to leave correspondingly treated laundry with a potential for irritation in very sensitive consumers. In addition, unwanted salt formation readily occurs in combination with anionic surfactants. For this reason, there is a strong interest in substitutes with none of these disadvantages.

One solution would be to replace the quaternary ammonium compounds by other cationic surfactants of the esterquat type. Although surfactants such as these have considerably better ecotoxicological compatibility and, in many cases, superior softening properties, their resistance to hydrolysis under the alkaline conditions of the washing process is limited so that they cannot be considered as genuine substitutes.

Accordingly, the problem addressed by the present invention was to provide new shaped detergents, preferably in the form of tablets, which would show satisfactory ecotoxicological compatibility and would be readily

soluble under washing conditions, would have adequate chemical resistance and, in particular, would provide laundry with an excellent soft feel.

**Description of the Invention**

The present invention relates to detergent tablets containing

(a) anionic, nonionic and/or amphoteric surfactants,
(b) non-enzymatic proteins and/or derivatives thereof,
(c) zeolites and
(d) disintegrating agents.

It has surprisingly been found that the detergent tablets according to the invention eminently satisfy the requirements stated above. The non-enzymatic proteins and protein derivatives are ideal substitutes for cationic surfactants because they produce comparable softness but at the same time are chemically stable, even under alkaline conditions, and give no cause for concern from either the ecological or the toxicological perspective. A particularly advantageous softening effect is observed in particular in combination with phosphates as builders and can be further improved by the addition of layer silicates (bentonites) or by the use of a surfactant system based on alkyl benzenesulfonates and alkyl sulfates. The detergents are preferably free from cationic surfactants.

Surfactants

The detergents may contain anionic, nonionic and/or amphoteric or zwitterionic surfactants as component (a). However, anionic surfactants or combinations of anionic and nonionic surfactants are preferably present. Typical examples of **anionic surfactants** are soaps, alkyl benzenesulfonates, alkane sulfonates, olefin sulfonates, alkyl ether sulfonates,

glycerol ether sulfonates, α-methyl ester sulfonates, sulfofatty acids, alkyl sulfates, fatty alcohol ether sulfates, glycerol ether sulfates, hydroxy mixed ether sulfates, monoglyceride (ether) sulfates, fatty acid amide (ether) sulfates, mono- and dialkyl sulfosuccinates, mono- and dialkyl sulfosuccinamates, sulfotriglycerides, amide soaps, ether carboxylic acids and salts thereof, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, N-acyl amino acids such as, for example, acyl lactylates, acyl tartrates, acyl glutamates and acyl aspartates, alkyl oligoglucoside sulfates, protein fatty acid condensates (especially wheat-based vegetable products) and alkyl (ether)phosphates. If the anionic surfactants contain polyglycol ether chains, the polyglycol ether chains may have a conventional homolog distribution, although they preferably have a narrow homolog distribution. Alkyl benzenesulfonates, alkyl sulfates, soaps, alkanesulfonates, olefin sulfonates, methyl ester sulfonates and mixtures thereof are preferably used.

Preferred **alkyl benzenesulfonates** preferably correspond to formula **(I)**:

$$\textbf{R-Ph-SO}_3\textbf{X} \qquad \textbf{(I)}$$

in which R is a branched, but preferably linear alkyl group containing 10 to 18 carbon atoms, Ph is a phenyl group and X is an alkali metal and/or alkaline earth metal, ammonium, alkylammonium, alkanolammonium or glucammonium. Of these alkyl benzenesulfonates, dodecyl benzenesulfonates, tetradecyl benzenesulfonates, hexadecyl benzenesulfonates and technical mixtures thereof in the form of the sodium salts are particularly suitable.

**Alkyl and/or alkenyl sulfates**, which are also often referred to as fatty alcohol sulfates, are understood to be the sulfation products of primary and/or secondary alcohols which preferably correspond to formula **(II)**:

$$R^2O\text{-}SO_3Y \qquad \textbf{(II)}$$

in which $R^2$ is a linear or branched, aliphatic alkyl and/or alkenyl group containing 6 to 22 and preferably 12 to 18 carbon atoms and Y is an alkali metal and/or alkaline earth metal, ammonium, alkylammonium, alkanolammonium or glucammonium. Typical examples of alkyl sulfates which may be used in accordance with the invention are the sulfation products of caproic alcohol, caprylic alcohol, capric alcohol, 2-ethylhexyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol and erucyl alcohol and the technical mixtures thereof, obtained by high-pressure hydrogenation of technical methyl ester fractions or aldehydes from Roelen's oxosynthesis. The sulfation products may advantageously be used in the form of their alkali metal salts, more especially their sodium salts. Alkyl sulfates based on $C_{16/18}$ tallow fatty alcohols or vegetable fatty alcohols with a comparable C-chain distribution in the form of their sodium salts are particularly preferred. In the case of branched primary types, the alcohols are oxoalcohols which are obtainable, for example, by addition of carbon monoxide and hydrogen onto $\alpha$-olefins by the Shop process. Corresponding alcohol mixtures are commercially available under the trade names of Dobanol® or Neodol®. Suitable alcohol mixtures are Dobanol 91®, 23®, 25® and 45®. Another possibility are the oxoalcohols obtained by the standard oxo process of Unichema or Condea in which carbon monoxide and hydrogen are added onto olefins. These alcohol mixtures are a mixture of highly branched alcohols and are commercially available under the name of Lial®. Suitable alcohol mixtures are Lial 91®, 111®, 123®, 125®, 145®.

Finally, **soaps** are understood to be fatty acid salts corresponding to

formula **(III):**

$$R^3CO\text{-}OX \qquad (III)$$

in which $R^3CO$ is a linear or branched, saturated or unsaturated acyl group containing 6 to 22 and preferably 12 to 18 carbon atoms and X is alkali and/or alkaline earth metal, ammonium, alkylammonium or alkanolammonium. Typical examples are the sodium, potassium, magnesium, ammonium and triethanolammonium salts of caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and technical mixtures thereof. Cocofatty acid or palm kernel oil fatty acid in the form of their sodium or potassium salts are preferably used.

Typical examples of **nonionic surfactants** are fatty alcohol polyglycol ethers, alkylphenol polyglycol ethers, fatty acid polyglycol esters, fatty acid amide polyglycol ethers, fatty amine polyglycol ethers, alkoxylated triglycerides, mixed ethers and mixed formals, alk(en)yl oligoglycosides, fatty acid-N-alkyl glucamides, protein hydrolyzates (more particularly wheat-based vegetable products), polyol fatty acid esters, sugar esters, sorbitan esters, polysorbates and amine oxides. If the nonionic surfactants contain polyglycol ether chains, the polyglycol ether chains may have a conventional homolog distribution, although they preferably have a narrow homolog distribution. Fatty alcohol polyglycol ethers, alkoxylated fatty acid lower alkyl esters or alkyl oligoglycosides are preferably used.

Preferred **fatty alcohol polyglycol ethers** correspond to formula **(IV):**

$$R^4O(CH_2CHR^5O)_nH \qquad (IV)$$

in which $R^4$ is a linear or branched alkyl and/or alkenyl group containing 6 to 22 and preferably 12 to 18 carbon atoms, $R^5$ is hydrogen or methyl and n is a number of 1 to 20. Typical examples are products of the addition of, on average, 1 to 20 and preferably 5 to 10 moles of ethylene and/or propylene oxide onto caproic alcohol, caprylic alcohol, 2-ethylhexyl alcohol, capric alcohol, lauryl alcohol, isotridecyl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, elaeostearyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol and brassidyl alcohol and technical mixtures thereof. Products of the addition of 3, 5 or 7 moles of ethylene oxide onto technical cocofatty alcohols are particularly preferred.

Suitable **alkoxylated fatty acid lower alkyl esters** are surfactants corresponding to formula **(V)**:

$$R^6CO\text{-}(OCH_2CHR^7)_mOR^8 \qquad \text{(V)}$$

in which $R^6CO$ is a linear or branched, saturated and/or unsaturated acyl group containing 6 to 22 carbon atoms, $R^7$ is hydrogen or methyl, $R^8$ is a linear or branched alkyl group containing 1 to 4 carbon atoms and m is a number of 1 to 20. Typical examples are the formal insertion products of, on average, 1 to 20 and preferably 5 to 10 moles of ethylene and/or propylene oxide into the methyl, ethyl, propyl, isopropyl, butyl and tert.butyl esters of caproic acid, caprylic acid, 2-ethylhexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid and erucic acid and technical mixtures thereof. The products are normally prepared by insertion of the alkylene oxides into the carbon ester

bond in the presence of special catalysts, for example calcined hydrotalcite. Reaction products of on average 5 to 10 moles of ethylene oxide into the ester bond of technical cocofatty acid methyl esters are particularly preferred.

**Alkyl and alkenyl oligoglycosides**, which are also preferred nonionic surfactants, normally correspond to formula **(VI)**:

$$R^9O\text{-}[G]_p \qquad \textbf{(VI)}$$

in which $R^9$ is an alkyl and/or alkenyl group containing 4 to 22 carbon atoms, G is a sugar unit containing 5 or 6 carbon atoms and p is a number of 1 to 10. They may be obtained by the relevant methods of preparative organic chemistry. **EP-A1 0 301 298** and **WO 90/03977** are cited as representative of the extensive literature available on the subject. The alkyl and/or alkenyl oligoglycosides may be derived from aldoses or ketoses containing 5 or 6 carbon atoms, preferably glucose. Accordingly, the preferred alkyl and/or alkenyl oligoglycosides are alkyl and/or alkenyl oligo**glucosides**. The index p in general formula **(VI)** indicates the degree of oligomerization (DP), i.e. the distribution of mono- and oligoglycosides, and is a number of 1 to 10. Whereas p in a given compound must always be an integer and, above all, may assume a value of 1 to 6, the value p for a certain alkyl oligoglycoside is an analytically determined calculated quantity which is generally a broken number. Alkyl and/or alkenyl oligoglycosides having an average degree of oligomerization p of 1.1 to 3.0 are preferably used. Alkyl and/or alkenyl oligoglycosides having a degree of oligomerization of less than 1.7 and, more particularly, between 1.2 and 1.4 are preferred from the applicational point of view. The alkyl or alkenyl radical $R^9$ may be derived from primary alcohols containing 4 to 11 and preferably 8 to 10 carbon atoms. Typical examples are butanol, caproic alcohol, caprylic alcohol, capric alcohol and undecyl alcohol and the

technical mixtures thereof obtained, for example, in the hydrogenation of technical fatty acid methyl esters or in the hydrogenation of aldehydes from Roelen's oxosynthesis. Alkyl oligoglucosides having a chain length of $C_8$ to $C_{10}$ (DP = 1 to 3), which are obtained as first runnings in the separation of technical $C_{8-18}$ coconut oil fatty alcohol by distillation and which may contain less than 6% by weight of $C_{12}$ alcohol as an impurity, and also alkyl oligo-glucosides based on technical $C_{9/11}$ oxoalcohols (DP = 1 to 3) are preferred. In addition, the alkyl or alkenyl radical $R^9$ may also be derived from primary alcohols containing 12 to 22 and preferably 12 to 14 carbon atoms. Typical examples are lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol, erucyl alcohol, brassidyl alcohol and technical mixtures thereof which may be obtained as described above. Alkyl oligoglucosides based on hydrogenated $C_{12/14}$ cocoalcohol with a DP of 1 to 3 are preferred.

Typical examples of **amphoteric or zwitterionic surfactants** are alkyl betaines, alkyl amidobetaines, aminopropionates, aminoglycinates, imidazolinium betaines and sulfobetaines. The surfactants mentioned are all known compounds. Information on their structure and production can be found in relevant synoptic works, for example in J. Falbe (ed.), "**Surfactants in Consumer Products**", Springer Verlag, Berlin, 1987, pp. 54-124 or J. Falbe (ed.), "**Katalysatoren, Tenside und Mineralöladditive (Catalysts, Surfactants and Mineral Oil Additives**", Thieme Verlag, Stuttgart, 1978, pp. 123-217. The detergents may contain the surfactants in quantities of 1 to 50% by weight, preferably 5 to 25% by weight and more particularly 10 to 20% by weight, based on the detergent.

<u>Non-enzymatic proteins and derivatives thereof</u>

Non-enzymatic proteins and derivatives thereof (component b), which are preferably protein hydrolyzates and/or protein fatty acid

condensates, are known substances which are used, for example, in skin-care preparations [cf. **Seifen-Fette-Öle-Wachse, 108, 177 (1982)**]. The addition "non-enzymatic" was chosen to distinguish the substances from typical detergent enzymes which are not used for the purposes of the invention. Typical examples of non-enzymatic **proteins** which may be used in the detergents according to the invention are keratin, elastin, collagen, wheat proteins, milk proteins, albumin proteins, silk proteins, almond proteins, soya proteins and other cereal proteins and also proteins from animal skins. **Protein hydrolyzates** are degradation products of these animal or vegetable proteins which are hydrolyzed by acid, alkaline and/or enzymatic hydrolysis and thereafter have an average molecular weight of 600 to 4,000 and preferably in the range from 2,000 to 3,500. Although protein hydrolyzates are not surfactants in the true sense insofar as they lack a hydrophobic residue, they are often used for formulating surface-active compositions by virtue of their dispersing properties. Overviews of the production and use of protein hydrolyzates have been published, for example, by G. Schuster and A. Domsch in **Seifen, Öle, Fette, Wachse, 108, 177 (1982)** and **Cosm. Toil. 99, 63 (1984)**, by H.W. Steisslinger in **Parf. Kosm. 72, 556 (1991)** and by F. Aurich et al. in **Tens. Surf. Det. 29, 389 (1992)**. **Protein fatty acid condensates** are obtained by reaction of the protein hydrolyzates mentioned with fatty acids which generally contain 6 to 22 and preferably 12 to 18 carbon atoms in the acyl group. The condensates are normally used in the form of their alkali metal, alkaline earth metal, ammonium, alkylammonium or alkanolammonium salts. Typical examples are the condensation products of wheat or soya protein hydrolyzates with caproic acid, caprylic acid, 2-ethyl hexanoic acid, capric acid, lauric acid, isotridecanoic acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, elaeostearic acid, arachic acid, gadoleic acid, behenic acid, erucic acid and technical mixtures thereof.

The detergents according to the invention may contain the proteins or protein derivatives in quantities of 0.1 to 10, preferably 1 to 8 and more particularly 3 to 5% by weight, based on the detergent.

Zeolites

The detergents according to the invention may contain zeolites as builders (component c). The finely crystalline, synthetic **zeolite** containing bound water often used as a detergent builder is preferably zeolite A and/or zeolite P. Zeolite MAP® (Crosfield) is a particularly preferred P-type zeolite. However, zeolite X and mixtures of A, X and/or P and also Y are also suitable. A co-crystallized sodium/potassium aluminium silicate of zeolite A and zeolite X commercially available as VEGOBOND AX® (from Condea Augusta S.p.A.) is also of particular interest. The zeolite may be used in the form of a spray-dried powder or even in the form of an undried stabilized suspension still moist from its production. Where the zeolite is used in the form of a suspension, the suspension may contain small additions of nonionic surfactants as stabilizers, for example 1 to 3% by weight, based on zeolite, of ethoxylated $C_{12-18}$ fatty alcohols containing 2 to 5 ethylene oxide groups, $C_{12-14}$ fatty alcohols containing 4 to 5 ethylene oxide groups or ethoxylated isotridecanols. Suitable zeolites have a mean particle size of less than 10 $\mu$m (volume distribution, as measured by the Coulter Counter method) and contain preferably 18 to 22% by weight and more preferably 20 to 22% by weight of bound water.

The zeolites are present in the final preparations in quantities of preferably 10 to 60 and more particularly 20 to 40% by weight, based on the detergent.

Disintegrating agents (disintegrators)

Disintegrating agents (component d) are substances which are added to the tablets to accelerate their disintegration on contact with water.

Disintegrators are reviewed, for example, in **J. Pharm. Sci.** 61 (9172) and in **Römpp Chemielexikon**, 9th Edition, Vol. 6, page 4440. Viewed macroscopically, the disintegrators may be homogeneously distributed in the tablet although, when observed under a microscope, they form zones of increased concentration due to their production. Preferred disintegrators include polysaccharides such as, for example, natural starch and derivatives thereof (carboxymethyl starch, starch glycolates in the form of their alkali metal salts, agar agar, guar gum, pectins, etc.), celluloses and derivatives thereof (carboxymethyl cellulose, microcrystalline cellulose), polyvinyl pyrrolidone, collodion, alginic acid and alkali metal salts thereof, amorphous or even partly crystalline layer silicates (bentonites), polyurethanes, polyethylene glycols and effervescent systems. Other examples of disintegrators which may be present in accordance with the invention can be found, for example, in **WO 98/40462** (Rettenmeyer), **WO 98/55583** and **WO 98/55590** (Unilever) and **WO 98/40463**, **DE 19709991** and **DE 19710254** (Henkel). Reference is specifically made to the teaching of these documents. The tablets may contain the disintegrators in quantities of 0.1 to 25% by weight, preferably in quantities of 1 to 20% by weight and more preferably in quantities of 5 to 15% by weight, based on the tablets.

Auxiliaries and additives

Other preferred ingredients of the detergents according to the invention are additional inorganic and organic builders, the inorganic builders used mainly being crystalline layer silicates and amorphous silicates with builder properties and - where permitted - phosphates, such as tripolyphosphates. The quantity of co-builder used should allow for the preferred quantities of zeolites.

Suitable substitutes or partial substitutes for phosphates and zeolites are **crystalline, layer sodium silicates** corresponding to the general

formula $NaMSi_xO_{2x+1} \cdot yH_2O$, where M is sodium or hydrogen, x is a number of 1.9 to 4 and y is a number of 0 to 20, preferred values for x being 2, 3 or 4. Crystalline layer silicates such as these are described, for example, in European patent application **EP 0 164 514 A1**. Preferred crystalline layer silicates corresponding to the above formula are those in which M is sodium and x assumes the value 2 or 3. Both β- and δ-sodium disilicates $Na_2Si_2O_5 \cdot yH_2O$ are particularly preferred, β-sodium disilicate being obtainable, for example, by the process described in International patent application **WO 91/08171**. Other suitable layer silicates are known, for example, from patent applications **DE 2334899 A1, EP 0026529 A1** and **DE 3526405 A1**. The suitability of these layer silicates is not limited to a particular composition or structural formula. However, smectites, more especially bentonites, are preferred for the purposes of the present invention. Suitable layer silicates which belong to the group of water-swellable smectites are, for example, those corresponding to the following general formulae:

| | |
|---|---|
| $(OH)_4Si_{8-y}Al_y(Mg_xAl_{4-x})O_{20}$ | montmorrilonite |
| $(OH)_4Si_{8-y}Al_y(Mg_{6-z}Li_z)O_{20}$ | hectorite |
| $(OH)_4Si_{8-y}Al_y(Mg_{6-z}Al_z)O_{20}$ | saponite |

where x = 0 to 4, y = 0 to 2 and z = 0 to 6. Small amounts of iron may additionally be incorporated in the crystal lattice of the layer silicates corresponding to the above formulae. In addition, by virtue of their ion-exchanging properties, the layer silicates may contain hydrogen, alkali metal and alkaline-earth metal ions, more particularly $Na^+$ and $Ca^{2+}$. The quantity of water of hydration is generally in the range from 8 to 20% by weight and is dependent upon the degree of swelling or upon the treatment method. Suitable layer silicates are known, for example, from **US 3,966,629 US 4,062,647, EP 0026529 A1** and **EP 0028432 A1**. Layer

silicates which, by virtue of an alkali treatment, are largely free from calcium ions and strongly coloring iron ions are preferably used.

Other preferred builders are **amorphous sodium silicates** with a modulus ($Na_2O$ : $SiO_2$ ratio) of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and more preferably 1:2 to 1:2.6 which dissolve with delay and exhibit multiple wash cycle properties. The delay in dissolution in relation to conventional amorphous sodium silicates can have been obtained in various ways, for example by surface treatment, compounding, compacting or by overdrying. In the context of the invention, the term "amorphous" is also understood to encompass "X-ray amorphous". In other words, the silicates do not produce any of the sharp X-ray reflexes typical of crystalline substances in X-ray diffraction experiments, but at best one or more maxima of the scattered X-radiation which have a width of several degrees of the diffraction angle. Particularly good builder properties may even be achieved where the silicate particles produce crooked or even sharp diffraction maxima in electron diffraction experiments. This may be interpreted to mean that the products have microcrystalline regions between 10 and a few hundred nm in size, values of up to at most 50 nm and, more particularly, up to at most 20 nm being preferred. So-called X-ray amorphous silicates such as these, which also dissolve with delay in relation to conventional waterglasses, are described for example in German patent application **DE-A-4400024 A1**. Compacted amorphous silicates, compounded amorphous silicates and overdried X-ray-amorphous silicates are particularly preferred.

The generally known phosphates may of course also be used as builders providing their use should not be avoided on ecological grounds. The sodium salts of the orthophosphates, the pyrophosphates and, in particular, the tripolyphosphates are particularly suitable. Their content is generally no more than 25% by weight and preferably no more than 20% by weight, based on the final detergent. In some cases, it has been found

that, in combination with other builders, tripolyphosphates in particular produce a synergistic improvement in multiple wash cycle performance, even in small quantities of up to at most 10% by weight, based on the final detergent.

Useful organic builders are, for example, the **polycarboxylic acids** usable in the form of their sodium salts, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids, aminocarboxylic acids, nitrilotriacetic acid (NTA), providing its use is not ecologically unsafe, and mixtures thereof. Preferred salts are the salts of the polycarboxylic acids, such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof. The acids per se may also be used. Besides their building effect, the acids also typically have the property of an acidifying component and, hence, also serve to establish a relatively low and mild pH value in detergents or cleaners. Citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and mixtures thereof are particularly mentioned in this regard.

Other suitable organic builders are **dextrins**, for example oligomers or polymers of carbohydrates which may be obtained by partial hydrolysis of starches. The hydrolysis may be carried out by standard methods, for example acid- or enzyme-catalyzed methods. The end products are preferably hydrolysis products with average molecular weights of 400 to 500,000. A polysaccharide with a dextrose equivalent (DE) of 0.5 to 40 and, more particularly, 2 to 30 is preferred, the DE being an accepted measure of the reducing effect of a polysaccharide by comparison with dextrose which has a DE of 100. Both maltodextrins with a DE of 3 to 20 and dry glucose sirups with a DE of 20 to 37 and also so-called yellow dextrins and white dextrins with relatively high molecular weights of 2,000 to 30,000 may be used. A preferred dextrin is described in British patent application **94 19 091 A1**. The oxidized derivatives of such dextrins are their reaction products with oxidizing agents which are capable of oxidizing

at least one alcohol function of the saccharide ring to the carboxylic acid function. Dextrins thus oxidized and processes for their production are known, for example, from European patent applications **EP 0 232 202 A1, EP 0 427 349 A1, EP 0 472 042 A1** and **EP 0 542 496 A1** and from International patent applications **WO 92/18542, WO 93/08251, WO 93/16110, WO 94/28030, WO 95/07303, WO 95/12619** and **WO 95/20608**. An oxidized oligosaccharide corresponding to German patent application **DE 196 00 018 A1** is also suitable. A product oxidized at $C_6$ of the saccharide ring can be particularly advantageous.

Other suitable co-builders are oxydisuccinates and other derivatives of **disuccinates**, preferably ethylenediamine disuccinate. The glycerol disuccinates and glycerol trisuccinates described, for example, in **US 4,524,009**, in **US 4,639,325**, in European patent application **EP 0 150 930 A1** and in Japanese patent application **JP 93/339896** are also particularly preferred in this connection. The quantities used in zeolite-containing and/or silicate-containing formulations are from 3 to 15% by weight.

Other useful organic **co-builders** are, for example, acetylated hydroxycarboxylic acids and salts thereof which may optionally be present in lactone form and which contain at least 4 carbon atoms, at least one hydroxy group and at most two acid groups. Co-builders such as these are described, for example, in International patent application **WO 95/20029**.

Suitable **polymeric polycarboxylates** are, for example, the sodium salts of polyacrylic acid or polymethacrylic acid, for example those with a relative molecular weight of 800 to 150,000 (based on acid and measured against polystyrenesulfonic acid). Suitable copolymeric polycarboxylates are, in particular, those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid. Acrylic acid/maleic acid copolymers containing 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid have proved to be particularly suitable. Their relative molecular weight, based on free acids, is generally in the range

from 5,000 to 200,000, preferably in the range from 10,000 to 120,000 and more preferably in the range from 50,000 to 100,000 (as measured against polystyrenesulfonic acid). The (co)polymeric polycarboxylates may be used either as powders or as aqueous solutions, 20 to 55% by weight aqueous solutions being preferred. Granular polymers are generally added to basic granules of one or more types in a subsequent step. Also particularly preferred are biodegradable polymers of more than two different monomer units, for example those which contain salts of acrylic acid and maleic acid and vinyl alcohol or vinyl alcohol derivatives as monomers in accordance with **DE 43 00 772 A1** or salts of acrylic acid and 2-alkylallyl sulfonic acid and sugar derivatives as monomers in accordance with **DE 42 21 381 C2**. Other preferred copolymers are those described in German patent applications **DE 43 03 320 A1** and **DE 44 17 734 A1** which preferably contain acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers. Other preferred builders are polymeric aminodicarboxylic acids, salts and precursors thereof. Polyaspartic acids and salts and derivatives thereof are particularly preferred.

Other suitable builders are **polyacetals** which may be obtained by reaction of dialdehydes with polyol carboxylic acids containing 5 to 7 carbon atoms and at least three hydroxyl groups, for example as described in European patent application **EP 0 280 223 A1**. Preferred polyacetals are obtained from dialdehydes, such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof and from polyol carboxylic acids, such as gluconic acid and/or glucoheptonic acid.

In addition, the detergents may contain components with a positive effect on the removability of oil and fats from textiles by washing. Preferred oil- and fat-dissolving components include, for example, nonionic cellulose ethers, such as methyl cellulose and methyl hydroxypropyl cellulose containing 15 to 30% by weight of methoxyl groups and 1 to 15% by weight of hydroxypropoxyl groups, based on the nonionic cellulose ether, and the

polymers of phthalic acid and/or terephthalic acid known from the prior art or derivatives thereof, more particularly polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives thereof. Of these, the sulfonated derivatives of phthalic acid and terephthalic acid polymers are particularly preferred.

Other suitable ingredients of the detergents are water-soluble inorganic salts, such as bicarbonates, carbonates, amorphous silicates, normal waterglasses with no pronounced builder properties or mixtures thereof. One particular embodiment is characterized by the use of alkali metal carbonate and/or amorphous alkali metal silicate, above all sodium silicate with a molar $Na_2O:SiO_2$ ratio of 1:1 to 1:4.5 and preferably 1:2 to 1:3.5. The sodium carbonate content of the final detergents is preferably up to 40% by weight and advantageously from 2 to 35% by weight. The content of sodium silicate (without particular building properties) in the detergents is generally up to 10% by weight and preferably between 1 and 8% by weight.

Besides the ingredients mentioned, the detergents may contain other known additives, for example salts of polyphosphonic acids, optical brighteners, enzymes, enzyme stabilizers, small quantities of neutral filler salts and dyes and perfumes and the like.

Among the compounds yielding $H_2O_2$ in water which serve as **bleaching agents**, sodium perborate tetrahydrate and sodium perborate monohydrate are particularly important. Other useful bleaching agents are, for example, sodium percarbonate, peroxypyrophosphates, citrate perhydrates and $H_2O_2$-yielding peracidic salts or peracids, such as perbenzoates, peroxophthalates, diperazelaic acid, phthaloiminoperacid or diperdodecanedioic acid. The content of bleaching agents in the detergents is preferably 5 to 35% by weight and more preferably up to 30% by weight, perborate monohydrate or percarbonate advantageously being used.

Suitable **bleach activators** are compounds which form aliphatic peroxocarboxylic acids containing preferably 1 to 10 carbon atoms and more preferably 2 to 4 carbon atoms and/or optionally substituted perbenzoic acid under perhydrolysis conditions. Substances bearing O- and/or N-acyl groups with the number of carbon atoms mentioned and/or optionally substituted benzoyl groups are suitable. Preferred bleach activators are polyacylated alkylenediamines, more particularly tetraacetyl ethylenediamine (TAED), acylated triazine derivatives, more particularly 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, more particularly tetraacetyl glycoluril (TAGU), N-acylimides, more particularly N-nonanoyl succinimide (NOSI), acylated phenol sulfonates, more particularly n-nonanoyl or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, more particularly phthalic anhydride, acylated polyhydric alcohols, more particularly triacetin, ethylene glycol diacetate, 2,5-diacetoxy-2,5-dihydrofuran and the enol esters known from German patent applications **DE 196 16 693 A1** and **DE 196 16 767 A1**, acetylated sorbitol and mannitol and the mixtures thereof (SORMAN) described in European patent application **EP 0 525 239 A1**, acylated sugar derivatives, more particularly pentaacetyl glucose (PAG), pentaacetyl fructose, tetraacetyl xylose and octaacetyl lactose, and acetylated, optionally N-alkylated glucamine and gluconolactone, and/or N-acylated lactams, for example N-benzoyl caprolactam, which are known from International patent applications **WO 94/27970, WO 94/28102, WO 94/28103, WO 95/00626, WO 95/14759** and **WO 95/17498**. The substituted hydrophilic acyl acetals known from German patent application **DE 196 16 769 A1** and the acyl lactams described in German patent application **DE 196 16 770** and in International patent application **WO 95/14075** are also preferably used. The combinations of conventional bleach activators known from German patent application **DE 44 43 177 A1** may also be used. Bleach activators such as these are present in the

usual quantities, preferably in quantities of 1% by weight to 10% by weight and more preferably in quantities of 2% by weight to 8% by weight, based on the detergent as a whole. In addition to or instead of the conventional bleach activators mentioned above, the sulfonimines known from European patents **EP 0 446 982 B1** and **EP 0 453 003 B1** and/or bleach-boosting transition metal salts or transition metal complexes may also be present as so-called bleach catalysts. Suitable transition metal compounds include, in particular, the manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes known from German patent application **DE 195 29 905 A1** and the N-analog compounds thereof known from German patent application **DE 196 20 267 A1**, the manganese-, iron-, cobalt-, ruthenium- or molybdenum-carbonyl complexes known from German patent application **DE 195 36 082 A1**, the manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands described in German patent application **DE 196 05 688**, the cobalt-, iron-, copper- and ruthenium-ammine complexes known from German patent application **DE 196 20 411 A1**, the manganese, copper and cobalt complexes described in German patent application **DE 44 16 438 A1**, the cobalt complexes described in European patent application **EP 0 272 030 A1**, the manganese complexes known from European patent application **EP 0 693 550 A1**, the manganese, iron, cobalt and copper complexes known from European patent **EP 0 392 592 A1** and/or the manganese complexes described in European patent **EP 0 443 651 B1** or in European patent applications **EP 0 458 397 A1, EP 0 458 398 A1, EP 0 549 271 A1, EP 0 549 272 A1, EP 0 544 490 A1** and **EP 0 544 519 A1**. Combinations of bleach activators and transition metal bleach catalysts are known, for example, from German patent application **DE 196 13 103 A1** and from international patent application **WO 95/27775**. Bleach-boosting transition metal complexes, more particularly with the central atoms Mn, Fe, Co. Cu, Mo. V, Ti and/or Ru, are used in typical quantities,

preferably in a quantity of up to 1% by weight, more preferably in a quantity of 0.0025% by weight to 0.25% by weight and most preferably in a quantity of 0.01% by weight to 0.1% by weight, based on the detergent as a whole.

Suitable **enzymes** are, in particular, enzymes from the class of hydrolases, such as proteases, esterases, lipases or lipolytic enzymes, amylases, cellulases or other glycosyl hydrolases and mixtures thereof. All these hydrolases contribute to the removal of stains, such as protein-containing, fat-containing or starch-containing stains, and discoloration in the washing process. Cellulases and other glycosyl hydrolases can contribute towards color retention and towards increasing fabric softness by removing pilling and microfibrils. Oxidoreductases may also be used for bleaching and for inhibiting dye transfer. Enzymes obtained from bacterial strains or fungi, such as Bacillus subtilis, Bacillus licheniformis, Streptomyces griseus and Humicola insolens are particularly suitable. Proteases of the subtilisin type are preferably used, proteases obtained from Bacillus lentus being particularly preferred. Of particular interest in this regard are enzyme mixtures, for example of protease and amylase or protease and lipase or lipolytic enzymes or protease and cellulase or of cellulase and lipase or lipolytic enzymes or of protease, amylase and lipase or lipolytic enzymes or protease, lipase or lipolytic enzymes and cellulase, but especially protease- and/or lipase-containing mixtures or mixtures with lipolytic enzymes. Examples of such lipolytic enzymes are the known cutinases. Peroxidases or oxidases have also been successfully used in some cases. Suitable amylases include in particular $\alpha$-amylases, isoamylases, pullanases and pectinases. Preferred cellulases are cellobiohydrolases, endoglucanases and $\beta$-glucosidases, which are also known as cellobiases, and mixtures thereof. Since the various cellulase types differ in their CMCase and avicelase activities, the desired activities can be established by mixing the cellulases in the appropriate ratios.

The enzymes may be adsorbed to supports and/or encapsulated in

membrane materials to protect them against premature decomposition. The percentage content of enzymes, enzyme mixtures or enzyme granules may be, for example, about 0.1 to 5% by weight and is preferably from 0.1 to about 2% by weight.

In addition to the monohydric and polyhydric alcohols, the detergents may contain other **enzyme stabilizers**. For example, 0.5 to 1% by weight of sodium formate may be used. Proteases stabilized with soluble calcium salts and having a calcium content of preferably about 1.2% by weight, based on the enzyme, may also be used. Apart from calcium salts, magnesium salts also serve as stabilizers. However, it is of particular advantage to use boron compounds, for example boric acid, boron oxide, borax and other alkali metal borates, such as the salts of orthoboric acid ($H_3BO_3$), metaboric acid ($HBO_2$) and pyroboric acid (tetraboric acid $H_2B_4O_7$).

The function of **redeposition inhibitors** is to keep the soil detached from the fibers suspended in the wash liquor and thus to prevent the soil from being re-absorbed by the washing. Suitable redeposition inhibitors are water-soluble, generally organic colloids, for example the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ether carboxylic acids or ether sulfonic acids of starch or cellulose or salts of acidic sulfuric acid esters of cellulose or starch. Water-soluble polyamides containing acidic groups are also suitable for this purpose. Soluble starch preparations and other starch products than those mentioned above, for example degraded starch, aldehyde starches, etc., may also be used. Polyvinyl pyrrolidone is also suitable. However, cellulose ethers, such as carboxymethyl cellulose (sodium salt), methyl cellulose, hydroxyalkyl cellulose, and mixed ethers, such as methyl hydroxyethyl cellulose, methyl hydroxypropyl cellulose, methyl carboxymethyl cellulose and mixtures thereof, and polyvinyl pyrrolidone are also preferably used, for example in quantities of 0.1 to 5% by weight, based on the detergent.

The detergents may contain derivatives of diaminostilbene disulfonic acid or alkali metal salts thereof as **optical brighteners**. Suitable optical brighteners are, for example, salts of 4,4'-bis-(2-anilino-4-morpholino-1,3,5-triazinyl-6-amino)-stilbene-2,2'-disulfonic acid or compounds of similar structure which contain a diethanolamino group, a methylamino group an anilino group or a 2-methoxyethylamino group instead of the morpholino group. Brighteners of the substituted diphenyl styryl type, for example alkali metal salts of 4,4'-bis-(2-sulfostyryl)-diphenyl, 4,4'-bis-(4-chloro-3-sulfostyryl)-diphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)-diphenyl, may also be present. Mixtures of the brighteners mentioned may also be used. Uniformly white granules are obtained if, in addition to the usual brighteners in the usual quantities, for example between 0.1 and 0.5% by weight and preferably between 0.1 and 0.3% by weight, the detergents also contain small quantities, for example $10^{-6}$ to $10^{-3}$% by weight and preferably around $10^{-5}$% by weight, of a blue dye. A particularly preferred dye is Tinolux® (a product of Ciba-Geigy).

Suitable **soil repellents** are substances which preferably contain ethylene terephthalate and/or polyethylene glycol terephthalate groups, the molar ratio of ethylene terephthalate to polyethylene glycol terephthalate being in the range from 50:50 to 90:10. The molecular weight of the linking polyethylene glycol units is more particularly in the range from 750 to 5,000, i.e. the degree of ethoxylation of the polymers containing polyethylene glycol groups may be about 15 to 100. The polymers are distinguished by an average molecular weight of about 5,000 to 200,000 and may have a block structure, but preferably have a random structure. Preferred polymers are those with molar ethylene terephthalate: polyethylene glycol terephthalate ratios of about 65:35 to about 90:10 and preferably in the range from about 70:30 to 80:20. Other preferred polymers are those which contain linking polyethylene glycol units with a molecular weight of 750 to 5,000 and preferably in the range from 1,000 to

about 3,000 and which have a molecular weight of the polymer of about 10,000 to about 50,000. Examples of commercially available polymers are the products Milease® T (ICI) or Repelotex® SRP 3 (Rhône-Poulenc).

Wax-like compounds may be used as **defoamers** in accordance with the present invention. "Wax-like" compounds are understood to be compounds which have a melting point at atmospheric pressure above 25°C (room temperature), preferably above 50°C and more preferably above 70°C. The wax-like defoamers are substantially insoluble in water, i.e. their solubility in 100 g of water at 20°C is less than 0.1% by weight. In principle, any wax-like defoamers known from the prior art may additionally be present. Suitable wax-like compounds are, for example, bisamides, fatty alcohols, fatty acids, carboxylic acid esters of monohydric and polyhydric alcohols and paraffin waxes or mixtures thereof. Alternatively, the silicone compounds known for this purpose may of course also be used.

Suitable **paraffin waxes** are generally a complex mixture with no clearly defined melting point. For characterization, its melting range is normally determined by differential thermoanalysis (DTA), as described in **"The Analyst"** 87 (1962), 420, and/or its solidification point is determined. The solidification point is understood to be the temperature at which the paraffin changes from the liquid state into the solid state by slow cooling. Paraffins which are entirely liquid at room temperature, i.e. paraffins with a solidification point below 25°C, are not suitable for use in accordance with the invention. It is possible, for example, to use the paraffin wax mixtures known from **EP 0309931 A1** of, for example, 26% by weight to 49% by weight of microcrystalline paraffin wax with a solidification point of 62°C to 90°C, 20% by weight to 49% by weight of hard paraffin with a solidification point of 42°C to 56°C and 2% by weight to 25% by weight of soft paraffin with a solidification point of 35°C to 40°C. Paraffins or paraffin mixtures which solidify at temperatures of 30°C to 90°C are preferably used. It is

important in this connection to bear in mind that even paraffin wax mixtures which appear solid at room temperature may contain different amounts of liquid paraffin. In the paraffin waxes suitable for use in accordance with the invention, this liquid component is as small as possible and is preferably absent altogether. Thus, particularly preferred paraffin wax mixtures have a liquid component at 30°C of less than 10% by weight and, more particularly, from 2% by weight to 5% by weight, a liquid component at 40°C of less than 30% by weight, preferably from 5% by weight to 25% by weight and more preferably from 5% by weight to 15% by weight, a liquid component at 60°C of 30% by weight to 60% by weight and preferably 40% by weight to 55% by weight, a liquid component at 80°C of 80% by weight to 100% by weight and a liquid component at 90°C of 100% by weight. In particularly preferred paraffin wax mixtures, the temperature at which a liquid component of 100% by weight of the paraffin wax is reached is still below 85°C and, more particularly, between 75°C and 82°C. The paraffin waxes may be petrolatum, microcrystalline waxes or hydrogenated or partly hydrogenated paraffin waxes.

**Bisamides** suitable as defoamers are those derived from saturated fatty acids containing 12 to 22 and preferably 14 to 18 carbon atoms and from alkylenediamines containing 2 to 7 carbon atoms. Suitable fatty acids are lauric acid, myristic acid, stearic acid, arachic acid and behenic acid and the mixtures thereof obtainable from natural fats or hydrogenated oils, such as tallow or hydrogenated palm oil. Suitable diamines are, for example, ethylenediamine, 1,3-propylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, p-phenylenediamine and toluylenediamine. Preferred diamines are ethylenediamine and hexamethylenediamine. Particularly preferred bisamides are bis-myristoyl ethylenediamine, bis-palmitoyl ethylenediamine, bis-stearoyl ethylenediamine and mixtures thereof and the corresponding derivatives of hexamethylenediamine.

Suitable **carboxylic acid esters** as defoamers are derived from carboxylic acids containing 12 to 28 carbon atoms. The esters in question are, in particular, esters of behenic acid, stearic acid, hydroxystearic acid, oleic acid, palmitic acid, myristic acid and/or lauric acid. The alcohol moiety of the carboxylic acid ester contains a monohydric or polyhydric alcohol containing 1 to 28 carbon atoms in the hydrocarbon chain. Examples of suitable alcohols are behenyl alcohol, arachidyl alcohol, cocoalcohol, 12-hydroxystearyl alcohol, oleyl alcohol and lauryl alcohol and ethylene glycol, glycerol, polyvinylvinyl alcohol, sucrose, erythritol, pentaerythritol, sorbitan and/or sorbitol. Preferred esters are esters of methanol, ethylene glycol, glycerol and sorbitan, the acid moiety of the ester being selected in particular from behenic acid, stearic acid, oleic acid, palmitic acid or myristic acid. Suitable esters of polyhydric alcohols are, for example, xylitol monopalmitate, pentaerythritol monostearate, glycerol monostearate, ethylene glycol monostearate and sorbitan monostearate, sorbitan palmitate, sorbitan monolaurate, sorbitan dilaurate, sorbitan distearate, sorbitan dibehenate, sorbitan dioleate and mixed tallow alkyl sorbitan monoesters and diesters. Suitable glycerol esters are the mono-, di- or triesters of glycerol and the carboxylic acids mentioned, the monoesters and diesters being preferred. Glycerol monostearate, glycerol monooleate, glycerol monopalmitate, glycerol monobehenate and glycerol distearate are examples. Examples of suitable natural esters as defoamers are beeswax, which mainly consists of the esters $CH_3(CH_2)_{24}COO(CH_2)_{27}CH_3$ and $CH_3(CH_2)_{26}COO(CH_2)_{25}CH_3$, and carnauba wax, carnauba wax being a mixture of carnauba acid alkyl esters, often in combination with small amounts of free carnauba acid, other long-chain acids, high molecular weight alcohols and hydrocarbons.

Suitable **carboxylic acids** as another defoamer compound are, in particular, behenic acid, stearic acid, oleic acid, palmitic acid, myristic acid and lauric acid and the mixtures thereof obtainable from natural fats or

optionally hydrogenated oils, such as tallow or hydrogenated palm oil. Saturated fatty acids containing 12 to 22 and, more particularly, 18 to 22 carbon atoms are preferred.

Suitable **fatty alcohols** as another defoamer compound are the hydrogenated products of the described fatty acids.

**Dialkyl ethers** may also be present as defoamers. The ethers may have an asymmetrical or symmetrical structure, i.e. they may contain two identical or different alkyl chains, preferably containing 8 to 18 carbon atoms. Typical examples are di-n-octyl ether, di-i-octyl ether and di-n-stearyl ether, dialkyl ethers with a melting point above 25°C and more particularly above 40°C being particularly suitable.

Other suitable defoamer compounds are **fatty ketones** which may be obtained by the relevant methods of preparative organic chemistry. They are produced, for example, from carboxylic acid magnesium salts which are pyrolyzed at temperatures above 300°C with elimination of carbon dioxide and water, for example in accordance with **DE 2553900 OS**. Suitable fatty ketones are produced by pyrolysis of the magnesium salts of lauric acid, myristic acid, palmitic aid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, arachic acid, gadoleic acid, behenic acid or erucic acid.

Other suitable defoamers are **fatty acid polyethylene glycol esters** which are preferably obtained by the homogeneously base-catalyzed addition of ethylene oxide onto fatty acids. The addition of ethylene oxide onto the fatty acids takes place in particular in the presence of alkanolamines as catalysts. The use of alkanolamines, especially triethanolamine, leads to extremely selective ethoxylation of the fatty acids, particularly where it is desired to produce compounds with a low degree of ethoxylation. Within the group of fatty acid polyethylene glycol esters, those with a melting point above 25°C and more particularly above 40°C are preferred.

Within the group of wax-like defoamers, the described paraffin waxes - in a particularly preferred embodiment - are used either on their own as wax-like defoamers or in admixture with one of the other wax-like defoamers, the percentage content of the paraffin waxes in the mixture preferably exceeding 50% by weight, based on the wax-like defoamer mixture. If necessary, the paraffin waxes may be applied to supports. Suitable support materials in the context of the present invention are any known inorganic and/or organic support materials. Examples of typical inorganic support materials are alkali metal carbonates, alumosilicates, water-soluble layer silicates, alkali metal silicates, alkali metal sulfates, for example sodium sulfate, and alkali metal phosphates. The alkali metal silicates are preferably a compound with a molar ratio of alkali metal oxide to $SiO_2$ of 1:1.5 to 1:3.5. The use of silicates such as these results in particularly good particle properties, more particularly high abrasion resistance and at the same time a high dissolving rate in water. Alumosilicates as a support material include, in particular, the zeolites, for example zeolite NaA and NaX. The compounds described as water-soluble layer silicates include, for example, amorphous or crystalline waterglass. Silicates commercially available as Aerosil® or Sipernat® may also be used. Suitable organic carrier materials are, for example, film-forming polymers, for example polyvinyl alcohols, polyvinyl pyrrolidones, poly(meth)acrylates, polycarboxylates, cellulose derivatives and starch. Suitable cellulose ethers are, in particular, alkali metal carboxymethyl cellulose, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose and so-called cellulose mixed ethers, for example methyl hydroxyethyl cellulose and methyl hydroxypropyl cellulose, and mixtures thereof. Particularly suitable mixtures are mixtures of sodium carboxymethyl cellulose and methyl cellulose, the carboxymethyl cellulose normally having a degree of substitution of 0.5 to 0.8 carboxymethyl groups per anhydroglucose unit while the methyl cellulose has a degree of substitution of 1.2 to 2 methyl

groups per anhydroglucose unit. The mixtures preferably contain alkali metal carboxymethyl cellulose and nonionic cellulose ether in ratios by weight of 80:20 to 40:60 and, more particularly, 75:25 to 50:50. Another suitable support is native starch which is made up of amylose and amylopectin. Native starch is starch obtainable as an extract from natural sources, for example from rice, potatoes, corn and wheat. Native starch is a standard commercial product and is therefore readily available. Suitable support materials are individual compounds or several of the compounds mentioned above selected in particular from the group of alkali metal carbonates, alkali metal sulfates, alkali metal phosphates, zeolites, water-soluble layer silicates, alkali metal silicates, polycarboxylates, cellulose ethers, polyacrylate/polymethacrylate and starch. Mixtures of alkali metal carbonates, more particularly sodium carbonate, alkali metal silicates, more particularly sodium silicate, alkali metal sulfates, more particularly sodium sulfate, and zeolites are particularly suitable.

Suitable **silicones** in the context of the present invention are typical organopolysiloxanes containing fine-particle silica which, in turn, may even be silanized. Corresponding organopolysiloxanes are described, for example, in European patent application **EP 0 496 510 A1**. Polydiorganosiloxanes known from the prior art are particularly preferred. However, siloxane-crosslinked compounds known to the expert as silicone resins may also be used. The polydiorganosiloxanes generally contain fine-particle silica which may even be silanized. Silica-containing dimethyl polysiloxanes are particularly suitable for the purposes of the present invention. The polydiorganosiloxanes advantageously have a Brookfield viscosity at 25°C of 5000 mPas to 30,000 mPas and, more particularly, 15,000 mPas to 25,000 mPas. The silicones are preferably applied to support materials. Suitable support materials were described above in connection with the paraffins. The support materials are generally present in quantities of 40 to 90% by weight and preferably in quantities of 45 to

75% by weight, based on defoamer.

Suitable **perfume oils or perfumes** include individual perfume compounds, for example synthetic products of the ester, ether, aldehyde, ketone, alcohol and hydrocarbon type. Perfume compounds of the ester type are, for example, benzyl acetate, phenoxyethyl isobutyrate, p-tert.butyl cyclohexyl acetate, linalyl acetate, dimethyl benzyl carbinyl acetate, phenyl ethyl acetate, linalyl benzoate, benzyl formate, ethyl methyl phenyl glycinate, allyl cyclohexyl propionate, styrallyl propionate and benzyl salicylate. The ethers include, for example, benzyl ethyl ether; the aldehydes include, for example, the linear alkanals containing 8 to 18 carbon atoms, citral, citronellal, citronellyloxyacetaldehyde, cyclamen aldehyde, hydroxycitronellal, lilial and bourgeonal; the ketones include, for example, the ionones, $\alpha$-isomethyl ionone and methyl cedryl ketone; the alcohols include anethol, citronellol, eugenol, geraniol, linalool, phenyl ethyl alcohol and terpineol and the hydrocarbons include, above all, the terpenes, such as limonene and pinene. However, mixtures of various perfumes which together produce an attractive perfume note are preferably used. Perfume oils such as these may also contain natural perfume mixtures obtainable from vegetable sources, for example pine, citrus, jasmine, patchouli, rose or ylang-ylang oil. Also suitable are clary oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil and ladanum oil and orange blossom oil, neroli oil, orange peel oil and sandalwood oil.

The perfumes may be directly incorporated in the detergents according to the invention, although it can also be of advantage to apply the perfumes to supports which strengthen the adherence of the perfume to the washing and which provide the textiles with a long-lasting fragrance through a slower release of the perfume. Suitable support materials are, for example, cyclodextrins, the cyclodextrin/perfume complexes optionally being coated with other auxiliaries.

If desired, the final preparations may also contain **inorganic salts** as fillers, such as sodium sulfate, for example, which is preferably present in quantities of 0 to 10% by weight and more particularly 1 to 5% by weight, based on the detergent.

Production of the detergent tablets

The production of the tablets is generally carried out by tabletting or press aglomeration. The particulate press agglomerates obtained may either be directly used as detergents or may be aftertreated beforehand by conventional methods. Conventional aftertreatments include, for example, powdering with fine-particle detergent ingredients which, in general, produces a further increase in bulk density. However, another preferred aftertreatment is the procedure according to German patent applications **DE 195 24 287 A1** and **DE 195 47 457 A1**, according to which dust-like or at least fine-particle ingredients (so-called fine components) are bonded to the particulate end products produced in accordance with the invention which serve as core. This results in the formation of detergents which contain these so-called fine components as an outer shell. Advantageously, this is again done by melt agglomeration. On the subject of the melt agglomeration of fine components, reference is specifically made to the disclosure of German patent applications DE-A-195 24 287 and DE-A-195 47 457. In the preferred embodiment of the invention, the solid detergents are present in tablet form, the tablets preferably having rounded corners and edges, above all in the interests of safer storage and transportation. The base of the tablets may be, for example, circular or rectangular in shape. Multilayer tablets, particularly tablets containing two or three layers which may even have different colors, are particularly preferred. Blue-white or green-white or blue-green-white tablets are particularly preferred. The tablets may also have compressed and non-compressed parts. Tablets with a particularly advantageous dissolving rate

are obtained if, before compression, the granular constituents contain less than 20% by weight and preferably less than 10% by weight of particles outside the 0.02 to 6 mm diameter range. A particle size distribution of 0.05 to 2.0 mm is preferred, a particle size distribution of 0.2 to 1.0 mm being particularly preferred.

## Examples

**Examples 1 to 6, Comparison Example C1.** In a Miele W 918 washing machine, 3.5 kg of standard laundry and a terry towel (which had been pretreated by washing twice with an all-purpose detergent) were washed at 90°C in a full wash cycle. Two detergent tablets (40 g) with the composition shown in Table 1 were placed in the dispensing compartment immediately before the test. After the wash cycle, the terry towel was dried for 24 hours at room temperature and then subjected to a panel test involving 20 people. Each person awarded a score of 1 to 4 (1 = hard, 4 = very soft). The average score represented the assessment of the products which is also shown in Table 1.

**Table 1.**

**Detergent composition and softness**

| Composition/performance | C1 | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| Dodecyl benzenesulfonate sodium salt | 4.0 | 4.0 | 4.0 | 4.0 | - | - | 4.0 |
| $C_{12/18}$ cocoalcohol sulfate sodium salt | 10.0 | 10.0 | 16.0 | 8.0 | - | - | 8.0 |
| $C_{12/18}$ cocofatty acid sodium salt | 2.0 | 2.0 | - | - | - | - | - |
| $C_{12/18}$ cocofatty alcohol + 7EO | 4.0 | 4.0 | - | - | - | - | - |
| $C_{12/14}$ cocoalkyl glucoside | - | - | - | 8.0 | 15.0 | 10.0 | 8.0 |
| $C_{12/18}$ cocoamphoacetate sodium salt | - | - | - | - | - | 10.0 | - |
| Zeolite A | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| Collagen cocofatty acid condensate sodium salt[1)] | - | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Layer silicate[2)] | - | - | - | - | - | - | 5.0 |
| Polycarboxylate[3)] | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Soda | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Sodium silicate | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 | 5.0 |
| Paraffin/silicone defoamer[4)] | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Microcrystalline cellulose | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 |
| Sodium sulfate | to 100 | | | | | | |
| ***Softness score*** | 1.0 | 2.0 | 2.5 | 2.5 | 3.0 | 2.5 | 3.0 |

1) Lamepon® SCE-B C 261 2) Bentone® EW 3) Sokalan® 760

4) Dehydran® 760